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**EP 0 361 494 A2** (54) Components and catalysts for the polymerization of olefins.

(57) Solid catalyst components for the polymerization of olefins modified with electron-donor compounds, comprising a titanium halide supported on a magnesium dihalide in active form and containing as an electron-donor compound a di- or polyether having specific reactivity characteristics towards  $MgCl_2$  and  $TiCl_4$ .

## COMPONENTS AND CATALYSTS FOR THE POLYMERIZATION OF OLEFINS

The present invention relates to solid components of catalysts for the polymerization of olefins and the catalysts obtained therefrom. The catalysts including titanium compounds supported on magnesium halides in active form are well known in the art.

Catalysts of this type are described for the first time in the USA patent No. 4,298,718. Said catalysts are formed on titanium tetrahalides supported on halides of magnesium in active form.

Although the catalysts have high activity in the polymerization of ethylene as well as alpha olefins like propylene and butene-1, they are not very stereospecific.

Improvements to stereospecificity have been made by adding electron-donor compounds to the solid catalyst component (U.S. patent No. 4,544,717).

Substantial improvements were made using, in addition to the electron-donor present in the solid component, an electron-donor added to the Al-alkyl co-catalyst component (U.S. patent No. 4,107,414).

The catalysts modified in this manner although they are highly stereospecific (isotactic index about 94-95) still do not show sufficiently high levels of activity.

Significant improvements in activity and stereospecificity were obtained by preparing the solid catalytic component according to the technique described in U.S. patent No. 4,226,741.

High level performance in catalyst activity as well as stereospecificity have been obtained with the catalysts described in European patent No. 045977. Said catalysts have as a solid catalyst component, a magnesium halide in active form on which is supported a titanium halide preferably  $\text{TiCl}_4$  and an electron-donor compound selected from specific classes of carboxylic acid esters, of which the phthalates are typical examples, and, as a co-catalyst component, a system formed of an Al-trialkyl compound and a silicon compound containing at least one Si-OR bond (R hydrocarbyl radical). After the appearance of the above mentioned patents which mark the fundamental step for the development of the coordination catalysts supported on magnesium halides, many patents have been filed with the purpose of modifying and/or improving the performance of the above mentioned catalysts.

In the prolific patent and scientific literature available, however, there is no description of catalysts endowed with both high activity and stereospecificity in which the electron-donor of the solid catalyst component is the only donor present in the catalyst system. The catalysts known up to now that have both high activity and stereospecificity always include the use of an electron-donor in the solid catalyst component and in the co-catalyst component.

Surprisingly, it has now been found that it is possible to prepare highly active and stereospecific catalysts where the only donor used is present in the solid catalyst component.

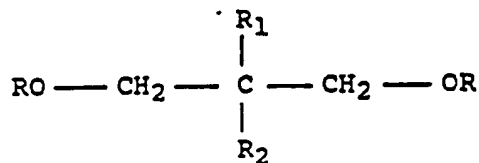
The donors used in the catalysts of this invention are ethers with two or more ether groups, which satisfy particular requisites of reactivity towards magnesium dichloride and titanium tetrachloride.

The ethers of the invention form complexes with magnesium dichloride but in a quantity of less than 60 mmoles per 100 g of  $\text{MgCl}_2$ ; with  $\text{TiCl}_4$  the ethers do not undergo at all substitution reactions or they react this way for less than 50% in moles.

Preferably the ethers form complexes with magnesium chloride in quantities comprised between 20 and 50 mmoles, and react with  $\text{TiCl}_4$  for less than 30%.

The procedures for the tests of magnesium chloride complexing and reaction with  $\text{TiCl}_4$  are reported below.

Examples of suitable ethers which satisfy the reactivity criterion set forth above are 1,3-dieethers of formula:



where R,  $\text{R}_1$  and  $\text{R}_2$  independently are linear or branched alkyl, cycloaliphatic, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, and  $\text{R}_1$  or  $\text{R}_2$  may also be hydrogen.

In particular R is an alkyl radical with 1-6 carbon atoms, and more specifically it is methyl. In this case, when  $\text{R}_1$  is methyl, ethyl, propyl or isopropyl,  $\text{R}_2$  may be ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, 2-

ethylhexyl, cyclohexyl methyl, phenyl, or benzyl; when R<sub>1</sub> is hydrogen R<sub>2</sub> can be ethyl, butyl, sec.butyl, t-butyl, 2-ethylhexyl, cyclohexylethyl, diphenylmethyl, p-chlorophenyl, 1-naphthyl, 1-decahydronaphthyl; R<sub>1</sub> and R<sub>2</sub> can be the same and be ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, neopentyl, isopentyl, phenyl, benzyl or cyclohexyl.

5 Examples of representative ethers that are included in the above formula are: 2-(2-ethylhexyl) 1,3-dimethoxypropane, 2-isopropyl- 1,3-dimethoxypropane, 2-butyl-1,3-dimethoxypropane, 2-sec-butyl-1,3-dimethoxypropane, 2-cyclohexyl-1,3-dimethoxypropane, 2-phenyl-1,3-diethoxypropane, 2-cumyl-1,3-diethoxypropane, 2-(2-phenylethyl)-1,3-dimethoxypropane, 2-(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-(p-chlorophenyl)-1,3-dimethoxypropane, 2-(diphenylmethyl)-1,3-dimethoxypropane, 2-(1-naphthyl)-1,3-dimethoxypropane, 2-(2-fluorophenyl)-1,3-dimethoxypropane, 2-(1-decahydronaphthyl)-1,3-dimethoxypropane, 2-(p-t-butylphenyl)-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2,2-diethyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2,2-dibutyl-1,3-dimethoxypropane, 2-methyl-2-propyl-1,3-dimethoxypropane, 2-methyl-2-benzyl-1,3-dimethoxypropane, 2-methyl-2-ethyl-1,3-dimethoxypropane, 2-methyl-2-propyl-1,3-dimethoxypropane, 2-methyl-2-phenyl-1,3-dimethoxypropane, 2-methyl-2-cyclohexyl-1,3-dimethoxypropane, 2,2-bis(p-chlorophenyl)-1,3-dimethoxypropane, 2,2-bis(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-methyl-2-isobutyl-1,3-dimethoxypropane, 2-methyl-2-(2-ethylhexyl)-1,3-dimethoxypropane, 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2,2-dibenzyl-1,3-dimethoxypropane, 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-diethoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2-isobutyl-2-isopropyl-1,3-dimethoxypropane, 2,2-di-sec-butyl-1,3-dimethoxypropane, 2,2-di-tert-butyl-1,3-dimethoxypropane, 2,2-di-neopentyl-1,3-dimethoxypropane, 2-isopropyl-2-isopentyl-1,3-dimethoxypropane, 2-phenyl-2-ethyl-1,3-dimethoxypropane, 2-cyclohexyl-2-cyclohexylmethyl-1,3-dimethoxypropane, 2-isopropyl-2-3,7-dimethyloctyl-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane, 2,2-diisopentyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2-heptyl-2-pentyl-1,3-dimethoxypropane.

Other suitable ethers are: 2,3-diphenyl-1,4-diethoxybutane, 2,3-dicyclohexyl-1,4-diethoxybutane, 2,2-dibenzyl-1,4-diethoxybutane, 2,3-dibenzyl-1,4-dimethoxybutane, 2,3-dicyclohexyl-1,4-dimethoxybutane, 2,3-diisopropyl-1,4-diethoxybutane, 2,2-bis(p-methylphenyl)-1,4-dimethoxybutane, 2,3-bis(p-chlorophenyl)-1,4-dimethoxybutane, 2,3-bis(p-fluorophenyl)-1,4-dimethoxybutane, 2,4-diphenyl-1,5-dimethoxypentane, 2,3-diphenyl-1,5-dimethoxypentane, 2,4-diisopropyl-1,5-dimethoxypentane, 3-methoxymethyltetrahydrofuran, 3-methoxymethyldioxane, 1,1-dimethoxymethyl-decahydronaphthalene, 1,1-dimethoxymethylindane, 2,2-dimethoxymethylindane, 1,1-dimethoxymethyl-2-isopropyl-5-methylcyclohexane, 1,3-diisoamyloxypropane, 1,2-diisobutoxypropane, 1,2-diisobutoxyethane, 1,3-diisoamyloxypropane, 1,2-diisoamuloxyethane, 1,3-dineopentoxypropane, 2,2-tetramethylene-1,3-dimethoxypropane, 1,2-dineopentoxyethane, 2,2-tetramethylene-1,3-dimethoxypropane, 2,2-pentamethylene-1,3-dimethoxypropane, 2,2-pentamethylene-1,3-dimethoxypropane, 2,2-hexamethylene-1,3-dimethoxypropane, 1,2-bis(methoxymethyl)cyclohexane, 2,8-dioxaspiro[5,5]undecane, 3,7-dioxabicyclo[3,3,1]nonane, 3,7-dioxabicyclo[3,3,0]octane, 3,3-diisobutyl-1,5-dioxanonane, 6,6-diisobutyldioxepane, 1,1-dimethoxymethylcyclopropane, 1,1-bis(dimethoxymethyl)cyclohexane, 1,1-bis(methoxymethyl)bicyclo[2,2,1]heptane, 1,1-dimethoxymethyl cyclopentane, 2-methyl-2-methoxymethyl-1,3-dimethoxypropane.

The ethers preferred are the 1,3-diethers belonging to the general formula indicated above and in particular those where R is methyl and R<sub>1</sub> and R<sub>2</sub>, independently, are isopropyl, isobutyl, t-butyl, cyclohexyl, isopentyl, cyclohexylethyl. Ethers particularly preferred are 2,2-diisobutyl-1,3-dimethoxypropane; 2-isopropyl 2-isopentyl-1,3-dimethoxypropane; 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane, 2-isopropyl-2-3,7-dimethyloctyl-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane, 2,2-diisopentyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2-heptyl-2-pentyl-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-isobutyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane.

The above ethers can be prepared according to the methods disclosed in Italian patent application No. 22 152 A/88 and in the European patent application ... .., Case HM 3854, of the same Applicant and filed on the same date as the present application with the title "Diethers Usable In The Preparation Of Ziegler-Natta Catalysts" (see enclosure A).

55 The ether complexing test with MgCl<sub>2</sub> is conducted as follows.

In a 100 ml glass flask with fixed blades glass mechanical agitator are introduced in a nitrogen atmosphere, in order:

- 70 ml anhydrous n-heptane

- 12 mmoles anhydrous  $\text{MgCl}_2$  activated as described below
- 2 mmoles ether:

The ingredients are heated at  $60^\circ\text{C}$  for 4 hours (stirring speed 400 rpm), then filtered and washed at room temperature with 100 ml n-heptane and dried with mechanical pump.

5 The quantity of ether complexed is determined, after treatment of the solid with 100 ml of ethanol by quantitative gaschromatic analysis.

The data relative to the complexing test are shown in Table 1.

The test for reactivity with  $\text{TiCl}_4$  is conducted as follows.

In a 25 ml test tube with a magnetic agitator are introduced, in a nitrogen atmosphere, in order:

- 10 - 10 ml anhydrous n-heptane
- 5 mmoles  $\text{TiCl}_4$
- 1 mmole ether donor

The ingredients are heated at  $70^\circ$  for 30 min then cooled at  $25^\circ\text{C}$  and decomposed with 90 ml of ethanol.

15 The solution obtained is analyzed gas chromatographically using a standard HIMONT method available upon request, with a Carlo Erba HRGC 5300 Mega Series gas chromatograph with a 25 meters Chrompack CP-SIL 5 CB capillary column. The data relative to the reactivity tests are shown in Table 1.

The magnesium dichloride used in the complexing test with the ethers is prepared as follows.

20 In a 1 l container of a vibrating mill (Siebtechnik's Vibratrom) containing 1.8 kg of steel spheres 16 mm in diameter, are introduced under a nitrogen atmosphere, 50 g anhydrous  $\text{MgCl}_2$  and 6.8 ml 1,2 dichloroethane (DCE).

The mixture is milled at room temperature for 96 hours, after which the solid obtained is dried at  $50^\circ\text{C}$  for 16 hours under vacuum of a mechanical pump.

25 Solid characterization.

In the X-ray powder spectrum:

- half peak breadth of D110 reflection = 1.15 cm;
- 30 - presence of a halo with maximum intensity at angle  $2\theta = 32.1^\circ$ ;
- Surface area (B.E.T.) = 125  $\text{m}^2/\text{g}$ ;
- Residual DCE = 2.5% by weight.

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Table 1

5	Ether	Complexing with MgCl <sub>2</sub> (*)	Reaction with TiCl <sub>4</sub> (**)
<hr/>			
	2,2-dimethyl-		
	1,3-dimethoxypropane	3,5	80
10	<hr/>		
	2-methyl-2-isopropyl-		
	1,3-dimethoxypropane	1,6	71
15	<hr/>		
	2,2-diisobutyl-		
	1,3-dimethoxypropane	3,3	98
20	<hr/>		
	2,2-diisobutyl-		
	1,3-diethoxypropane	2,0	100
25	<hr/>		
	2,2-diisobutyl-		
	1,3-di-n-butoxypropane	0,5	97
30	<hr/>		
	2,2-diphenyl-		
	1,3-dimethoxypropane	0,7	75
35	<hr/>		
	2,2-bis (cyclohexylmethyl)-		
	1,3-dimethoxypropane	1,8	85
40	<hr/>		
	1,3-diisobutoxypropane	2,6	99
45	<hr/>		

50

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Table 1 (follow)

5	2,2-pentamethylene-		
	1,3-dimethoxypropane	2,4	100
10	-----		
	1,1-bis(methoxymethyl )		
	bicyclo-(2,2,1-heptane)	1,9	93
15	-----		
	1,3 dimethoxypropane	9,6	100
	-----		
20	1-isopropyl-2,2-dimethyl-		
	1,3-dimethoxypropane	1,3	0
	2-isopentyl-2-isopropyl		
25	1,3-dimethoxypropane	2,5	98
	-----		
	1,2 dimethoxyethane	9,4	76
30	=====		

(\*) Moles of ether X 100 complexed by 100 g of MgCl<sub>2</sub>

(\*\*) Percentage in moles of ether recovered after reaction with  
TiCl<sub>4</sub>

The preparation of the solid catalyst component including the ethers of the invention is carried out according to various methods.

For example, the magnesium dihalide (used in anhydrous state containing less than 1% of water), the titanium compound and the di or polyether are ground together under conditions where activation of the magnesium dihalide occurs. The milled product is then treated one or more times with TiCl<sub>4</sub> in excess at temperatures between 80 and 135° C and then washed repeatedly with a hydrocarbon i.e. hexane until all chlorine ions disappear.

According to another method, the anhydrous magnesium dihalide is preactivated according to known methods in the prior art and then reacted with an excess of TiCl<sub>4</sub> which contains the ether compound in solution, at temperatures between 80 and 135° C. The treatment with TiCl<sub>4</sub> is repeated and the solid is then washed with hexane to eliminate all traces of unreacted TiCl<sub>4</sub>.

According to another method, an MgCl<sub>2</sub> nROH adduct (particularly in form of spheroidal particles) in which n is a number from 1 to 3, and ROH is ethanol, butanol, or isobutanol, is treated with an excess of TiCl<sub>4</sub> containing the ether compound in solution at a temperature generally between 80 and 120° C. After the reaction, the solid is treated once more with TiCl<sub>4</sub>, then separated and washed with a hydrocarbon until the chlorine ions are removed.

According to another method, carboxylates or halocarboxylates of magnesium or alcoholates or chloroalcoholates of magnesium, the chloroalcoholates prepared according to U.S. patent No. 4,220,554 are treated with TiCl<sub>4</sub> in excess containing the ether compound in solution, under reaction conditions described

above.

According to another method complexes of magnesium halide with titanium alcoholates for example the complex  $\text{MgCl}_2 \cdot 2\text{Ti}(\text{OC}_4\text{H}_9)_4$  are treated, in a hydrocarbon solution, with  $\text{TiCl}_4$  in excess containing the ether compound in solution. The solid product is separated and further treated with an excess of  $\text{TiCl}_4$  and then separated and washed with hexane. The reaction with  $\text{TiCl}_4$  is conducted at temperatures between 80 and 120° C.

According to a variant of the above method, the complex between  $\text{MgCl}_2$  and the titanium alcoholate is reacted in hydrocarbon solution with hydropolyxyloxane. The separated solid product is reacted at 50° C with silicon tetrachloride containing the ether compound in solution and the solid is treated with  $\text{TiCl}_4$  in excess operating at 80-100° C. It is possible to react with  $\text{TiCl}_4$ , in excess, containing the ether compound in solution, porous styrene-divinylbenzene resins in spherical particle form, impregnated with solutions of compounds or complexes of Mg soluble in organic solvents.

The resins and their method of impregnation are described in U.S. patent application S.N. 07/359,234.

The reaction with  $\text{TiCl}_4$  is carried out at 80-100° C and after separating the  $\text{TiCl}_4$  excess, the reaction is repeated and the solid is then washed with a hydrocarbon.

The molar ratio  $\text{MgCl}_2$ /ether compound used in the reactions indicated above is generally between 4:1 and 12:1.

The ether compound is fixed on the magnesium halide containing component in quantities generally between 5 and 20% mole.

However, in the case of components supported on resins, the molar ratio between fixed ether compound and the magnesium present in generally between 0.3 and 0.8.

In the catalytic components of the invention the ratio Mg/Ti is generally between 30:1 and 4:1; in the components supported on resins the ratio is lower, generally from 2:1 to 3:1.

The titanium compounds that can be used for the preparation of catalytic components are the halides and halogen alcoholates. Titanium tetrachloride is the preferred compound. Satisfactory results are obtained also with trihalides, particularly  $\text{TiCl}_3 \cdot \text{HR}$ ,  $\text{TiCl}_3 \cdot \text{ARA}$ , and with haloalcoholates, such as  $\text{TiCl}_3 \cdot \text{OR}$ , where R is a phenyl radical.

The above mentioned reactions result in the formation of magnesium dihalide in active form.

In addition to these reactions, other reactions that result in the formation of magnesium dihalide in active form starting with magnesium compounds different from halides are well known in literature.

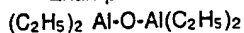
The active magnesium dihalides present in the solid catalyst components of the invention show in the X-ray powder spectrum of the catalyst component the replacement of the most intense diffraction present in the powder spectrum of the non-activated magnesium halides having a surface area of less than 3 m<sup>2</sup>/g by a halo with the maximum intensity peak shifted with respect to the position of the most intense diffraction line, or a half peak breadth of the most intense diffraction line at least 30% greater than the half peak breadth of the corresponding line of the non-activated magnesium halide. The most active forms are those where in the X-ray powder spectrum of the catalyst component a halo appears.

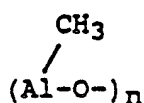
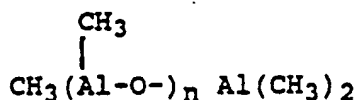
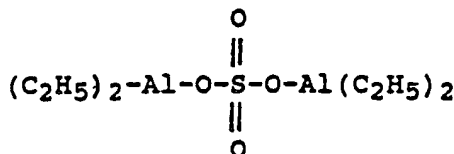
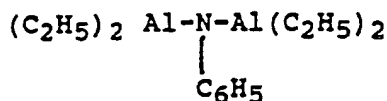
Among the magnesium dihalides, the magnesium dichloride is the preferred compound. In the case of the most active forms of magnesium dichloride the halo appears in place of the diffraction line that is present in the spectrum of the non-active magnesium chloride at an interplanar distance of 2.56 Å.

The solid catalyst component of the invention form, by reaction with Al-alkyl compounds, catalysts for the polymerization of olefins  $\text{CH}_2 = \text{CHR}$ , where R is hydrogen, alkyl radical with 1-6C, or aryl radical, or mixtures of said olefins mixed with each other with or without diolefins.

The Al-alkyl compounds include Al-trialkyl such as Al-triethyl, Al-triisobutyl, Al-tri-n-butyl. Linear or cyclic Al-alkyl compounds containing two or more Al atoms linked to each other by O, N or S atoms may be used.

Examples of these compounds are:





where n is a number between 1 and 20.

Also one can use  $\text{AlR}_2\text{OR}'$  compounds, where  $\text{R}'$  is an aryl radical substituted in position 2 and/or 6 and R is an alkyl radical with 1-6 carbon atoms, or  $\text{AlR}_2\text{H}$  compounds.

The Al-alkyl compound is used in Al/Ti ratios generally between 1 and 1000.

The trialkyl compounds may be used in mixtures with Al-alkyl halides, such as  $\text{AlEt}_2\text{Cl}$ .

The polymerization of olefins is carried out according to known methods in a liquid phase of the monomer(s) or a solution of monomer(s) in an aliphatic or aromatic hydrocarbon solvent, or in gas phase, or with techniques using a combination of liquid phase and gas phase.

The (co)polymerization temperature is generally between  $0^\circ$  and  $150^\circ\text{C}$ , preferably between  $60^\circ$  and  $100^\circ\text{C}$ , while operating at atmospheric pressure or at a higher pressure.

The catalysts may be precontacted with small quantities of olefins (prepolymerization). The prepolymerization improves the catalyst performance as well as the polymer morphology.

The prepolymerization is carried out by maintaining the catalyst in suspension in a hydrocarbon solvent (hexane, heptane, etc.) while contacting small amounts of the monomer with the catalyst and polymerizing at a temperature between room temperature and  $60^\circ\text{C}$  producing quantities of polymer included between 0.5 and 3 times the weight of the catalyst component. It may also be carried out in liquid or gaseous monomer, under the temperature conditions above, to produce quantities of polymer up to 1000 g per g of the catalyst component.

In case of stereoregular polymerization of olefins, in particular of propylene, some times it is convenient to use together with the Al-alkyl compound an electron-donor selected from 2,2,6,6-tetramethylpiperidine and silicon compounds containing at least one Si-OR bond wherein R is a hydrocarbyl radical.

Preferably the silicon compounds have the formula  $\text{R}^{\text{I}}\text{R}^{\text{II}}\text{Si}(\text{OR}^{\text{III}})(\text{OR}^{\text{IV}})$

where  $\text{R}^{\text{I}}$  and  $\text{R}^{\text{II}}$  independently, are branched alkyl, cycloaliphatic or aryls radicals with 1-12 carbon atoms;  $\text{R}^{\text{III}}$  and  $\text{R}^{\text{IV}}$  independently are alkyl radicals with 1-6 carbon atoms.

Examples of such compounds are:

$(t\text{-butyl})_2\text{Si}(\text{OC}_3)_2$ ;  $(\text{cyclohexyl})_2\text{Si}(\text{OCH}_3)_2$ ;  $(\text{isopropyl})_2\text{Si}(\text{OCH}_3)_2$ ;  $(\text{sec-butyl})_2\text{Si}(\text{OCH}_3)_2$ .

The molar ratio between Al-alkyl compound and electron-donor is usually between 5:1 and 100:1.

As indicated above, the catalysts find particular application in the polymerization of  $\text{CH}_2=\text{CHR}$  olefins where R is an alkyl radical with 1-6 carbon atoms or an aryl radical.

They are also particularly suited for the polymerization of ethylene and its mixtures with smaller proportions of alpha-olefins, such as butene-1, hexene-1 and octene-1 to form LLDPE, because the catalysts produce polymers with narrow molecular weight distribution.

In the copolymerization of ethylene with propylene, or other alpha-olefins or mixtures thereof to form elastomeric products copolymers are obtained having low crystallinity suitable therefore for the production of elastomers with highly valued qualities.

The following examples illustrate the invention.



In the examples, unless otherwise indicated, the percentages are by weight.

The solubility in xylene is determined by thermo solubilizing the polymer (130 °C), cooling and then filtering it.

The solubility is determined by the fraction soluble at 25 °C. The insoluble residue substantially corresponds to the isotacticity index determined by extraction with boiling n-heptane (4 hours). Melt index E and F for polyethylene and L for polypropylene are determined according to ASTM D1238. Melt index E and F are measured at 190 °C with respective weights of 2.15 and 21.6 Kg. The one for polypropylene is measured at 230 °C with a weight of 2.16 Kg.

The intrinsic viscosity are determined in tetralin at 135 °C. Unless otherwise indicated, the isotacticity index (I.I.) has been determined by extraction with boiling n-heptane (4 hours).

### Polymerization Procedure

#### A In liquid monomer

##### Procedure A.1.

In a 4 l stainless steel autoclave equipped with an anchor agitator and previously purged with nitrogen flux at 70 °C for 1 hour, were introduced, under propylene flow at 30 °C, 80 ml anhydrous n-hexane containing an adequate quantity of solid catalyst component and 6.9 mmoles of  $\text{Al}(\text{Et})_3$ . The autoclave was closed and 120 ml of hydrogen was introduced. The agitator was inserted and 1.2 Kg of liquid propylene, or other alpha-olefin monomer capable of being polymerized in liquid phase, was charged. The temperature was brought to 70 °C in 5 minutes and the polymerization was carried out for 2 hours. At the end of the test the unreacted propylene is removed, the polymer recovered and dried in an oven at 70 °C under nitrogen flow for 3 hours, and then characterized.

##### Procedure A.1.1.

The procedure of A.1 above were followed except that added to the hexane was an appropriate quantity of an electron-donor together with  $\text{Al}(\text{Et})_3$  corresponding to a molar ratio  $\text{Al}/\text{donor} = 20$ . The composition of the solid catalyst components and the ethers used, the polymerization yields and the properties of the polymers obtained are described in tables 2 and 3.

In table 3 the donor used together with  $\text{Al}(\text{Et})_3$  is indicated in parenthesis.

#### B In solvent.

##### Procedure B.2.

A 2.5 l stainless steel autoclave, equipped with a thermostat and magnetic agitator, which was previously purged with nitrogen flux at 70 °C for 1 hour and washed 4 times successively with propylene, was heated to 45 °C and, under a light nitrogen flow, 870 ml of anhydrous hexane was charged. The catalyst suspension (catalyst component and Al-alkyl premixed immediately before the test in 130 ml solvent) was then added. The autoclave was closed and 120 ml of hydrogen was fed from a calibrated cylinder. The agitator was inserted and the temperature was rapidly brought to 75 °C (in about 5 minutes). Gaseous propylene or other alpha-olefin monomer was then introduced up to a total pressure of 8 atm.

This condition was maintained for 4 hours continuously feeding propylene or other monomers to reintegrate the monomer polymerized. At the end of the polymerization the autoclave was rapidly degassed and cooled to 25-30 °C. The polymer suspension was then filtered, the solid part was dried in an oven at 70 °C in nitrogen for 4 hours and then weighed and analyzed. The filtrate was evaporated and the dry residue consisting of amorphous polymer was recovered and weighed. This was taken into consideration in calculating the total yield and the total isotactic index.

Procedure B.2.1

In a 2000 ml stainless steel autoclave, equipped with an anchor agitator, was introduced under a propylene flow at 25 °C 1000 ml n-heptane, 2.5 mmoles of  $\text{Al}(\text{C}_2\text{H}_5)_3$  and an adequate quantity of the solid catalyst component. The autoclave was closed and the pressure brought to 1 atm. while feeding propylene, and an overpressure of hydrogen equal to 0.2 atm was introduced. The reaction mixture was heated to 70 °C and the pressure brought to a total of 7 atm, by feeding propylene, and polymerized for 2 hours while continuing to feed the monomer to maintain the pressure at 7 atm.

The polymer obtained was isolated by filtration and dried; the polymer remaining in the filtrate was precipitated in methanol, vacuum dried and considered in determining the total insoluble residue of the extraction with n-heptane. The composition of the solid catalyst components and ethers used and the polymerization yields and the properties of the polymers obtained are described in tables 2 and 3.

Procedure B.2.2.

The polymerization methods described in procedure B.2.1. were followed except using 5 mmoles of  $\text{Al}(\text{C}_2\text{H}_5)_3$  together with an adequate quantity of electron donor such that the molar ratio  $\text{Al}/\text{donor} = 20$ . The composition of the solid catalyst components, ether and electron donor (with the Al-alkyl compound) used and the polymerization yields and the properties of the polymers obtained are described in tables 2 and 3. In table 3 the donor used together with  $\text{Al}(\text{C}_2\text{H}_5)_3$  is indicated in parenthesis.

Example 1

In a 1 l flask equipped with condenser, mechanical agitator and thermometer was introduced 625 ml  $\text{TiCl}_4$  under nitrogen environment. 25 g of spherical  $\text{MgCl}_2 \cdot 2.1\text{C}_2\text{H}_5\text{OH}$  support, obtained according to the procedures and ingredients of example 1 of U.S. patent 4 469 648, was fed at 0 °C with agitation and heated to 100 °C over 1 hour. When the temperature reached 40 °C, 4.1 ml of 2,2-diisobutyl-1,3-dimethoxypropane was introduced, and the contents maintained at 100 °C for 2 hours, left to settle and the supernatant siphoned off. 550 ml of  $\text{TiCl}_4$  was added to the solid and heated at 120 °C for 1 hour with agitation. The agitation was stopped, the solid was allowed to settle and the supernatant was removed by siphon. The residual solid was then washed 6 times with 200 ml portions of anhydrous hexane at 60 °C and 3 times at room temperature and dried under vacuum.

The catalyst solid component contained 3.45% Ti and 12.6% 2,2-diisobutyl-1,3-dimethoxypropane. Propylene was polymerized according to procedure A.1 above for the liquid monomer using 0.76 g of  $\text{Al}(\text{C}_2\text{H}_5)_3$ , 0.09 ml of hexane suspension containing 7.25 mg of solid catalyst component and 1000 ml hydrogen. 460 g of polymer was obtained. The polymer yield was 63.4 Kg/g of catalyst component. The polymer has a 95.3% insoluble residue in xylene at 25 °C, a melt index of 10.0 g/10' and a tamped bulk density of 0.48 g/ml.

Example 2

In a 500 ml glass flask equipped with condenser, mechanical agitator and thermometer, was introduced, in an anhydrous nitrogen environment at 20 °C, 285 ml of  $\text{TiCl}_4$  and 20 g of  $\text{C}_2\text{H}_5\text{OMgCl}$  support prepared according to the procedure of U.S. patent n. 4,220,554. While agitating the contents were heated to 70 °C in 30 minutes and then 4.7 ml 2,2-diisobutyl-1,3-dimethoxypropane was added and heated to 120 °C in 30 minutes. The temperature was maintained at 120 °C for 1 hour. The reaction mixture was allowed to settle and supernatant removed by siphon. Then another 285 ml  $\text{TiCl}_4$  were added and heated at 120 °C for 1 hour. The reaction mixture was allowed to settle and the supernatant removed by siphon. The residual solids were washed 5 times with 150 ml portions of anhydrous heptane at 80 °C, and again at room temperature with 150 ml portions of anhydrous hexane until there were no chlorine ions in the wash liquid.

The analysis of the vacuum dried solid catalyst component showed a content of 2.2% Ti and 12.2% 2,2-diisobutyl-1,3-dimethoxypropane.

Propylene was polymerized according to the Procedure A.1 above using 0.76 g  $\text{Al}(\text{C}_2\text{H}_5)_3$ , 0.12 ml hexane suspension containing 13 mg of solid catalyst component and 1000 ml hydrogen.

240 g of polymer was obtained with a polymer yield of 18.4 Kg/g catalyst component, a 95.2%

insoluble residue in xylene, at 25 °C, a melt index of 10.6 g/10' and a tamped bulk density of 0.50 g/ml.

### Example 3

5 In a 350 ml porcelain jar containing 4 porcelain spheres, was introduced, under an anhydrous nitrogen environment, 9.2 g of commercial anhydrous  $MgCl_2$  and 3.3 ml of 2,2-diisobutyl-1,3-dimethoxypropane. The jar is placed in a centrifugal mill operated at 350 rpm for 15 hours.

10 In a 250 ml glass flask fitted with a condenser, mechanical agitator and thermometer, under an anhydrous nitrogen environment at room temperature, were introduced 8 g of the above milled product and 115 ml of  $TiCl_4$ .

The contents were heated to 120 °C in 20 minutes and maintained at 120 °C for 2 hours.

15 The solids were allowed to settle and supernatant was siphoned off. Another 115 ml of  $TiCl_4$  was introduced, heated at 120 °C for 2 hour. The solids were allowed to settle and the supernatant removed by siphon. The solid residue was washed repeatedly at 60 °C and at 40 °C with 100 ml portions of anhydrous hexane, until there were no chlorine ions in the wash liquid. The solid residue, obtained by vacuum drying, contained 2.15% Ti and 10.2% 2,2-diisobutyl-1,3-dimethoxypropane. The polymerization was carried out according to procedure B.2, using 0.57 g  $Al(C_2H_5)_3$  and 0.25 ml hexane suspension containing 15.0 mg of  
20 solid catalyst component. 284 g of polymer was obtained with a polymer yield of 18.9 Kg/g catalyst, a 96.1% residue insoluble in xylene at 25 °C, a melt index of 4.2 g/10' and a tamped bulk density of 0.35 g/ml.

### 25 Example 4

In a 350 ml porcelain jar containing 4 porcelain spheres was introduced, under an anhydrous nitrogen environment, 7.65 of anhydrous  $MgCl_2$ , 2.76 ml 2,2-diisobutyl-1,3- dimethoxypropane, and 1.17 ml  $TiCl_4$ . The jar was placed in a centrifugal mill operated at 350 rpm for 20 hours. In a 350 ml glass reactor,  
30 equipped with porous disk for filtration, condenser, mechanical agitator and thermometer, was introduced at room temperature under an anhydrous nitrogen environment, 8 g of the above milled product and 32 ml 1,2-dichloroethane. The contents were heated at 83 °C for 2 hours, then filtered and the solid residue washed 3 times with 50 ml portions of anhydrous hexane. The solid residue obtained by vacuum drying contained 1.5% Ti and 18.4% 2,2-diisobutyl-1,3-dimethoxypropane. Propylene was polymerized according  
35 to procedure B.2 using 0.57 g  $Al(C_2H_5)_3$  and 0.5 ml hexane suspension containing 81 mg solid catalyst component. 188 g of polymer was obtained with polymer yield of 2.3 Kg/g catalyst component, a 94.7% residue insoluble in xylene, at 25 °C a melt index of 8.4 g/10' , and tamped bulk density of 0.29 g/ml.

### 40 Example 5

In a 500 ml glass flask equipped with a condenser, mechanical agitator and thermometer, was introduced, at room temperature under anhydrous nitrogen atmosphere, 250 ml of  $TiCl_4$  and 25 g of support in spherical particles comprising a styrene-divinylbenzene copolymer impregnated with the  $MgCl_2$  2Ti-  
45  $(OC_4H_9)_4$  complex, prepared according to procedure of example 1 of U.S. patent application SN 07/359,234.

While agitating, the contents were heated to 100 °C. When the temperature reaches 40 °C, 1.52 ml of 2,2-diisobutyl-1,3-dimethoxypropane was introduced. The temperature maintained at 100 °C for 1 hour, the solid allowed to settle and the supernatant was removed by siphon. An additional 250 ml  $TiCl_4$  was fed and  
50 heated at 120 °C for 2 hours. After settlement of the solids and siphoning of the supernatant, the solid residue was washed 5 times with 150 ml portions of anhydrous heptane at 85 °C, then 3 times with anhydrous hexane at room temperature, until no chlorine ions were formed in the wash liquid.

After vacuum drying, the solid catalytic component contained 0.77% Ti and 3.9% 2,2-diisobutyl-1,3-dimethoxypropane. Propylene was polymerized according to procedure A.1 using 0.79 g  $Al(C_2H_5)_3$ , 1.4 ml  
55 hexane suspension containing 49.5 mg solid catalyst component and 1300 ml hydrogen. 400 g of polymer was obtained with a polymer yield of 8.1 kg/g catalyst component, a 95.1% insoluble residue in xylene, at 25 °C, a melt index of 11.2 g/10' and a tamped bulk density of 0.42 g/ml.

Example 6

In a 500 ml glass flask equipped with condenser, mechanical agitator and thermometer was introduced 156.9 ml  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  and 20 g anhydrous  $\text{MgCl}_2$ . While agitating, the contents were heated to  $140^\circ\text{C}$  for 3 hours, cooled to  $40^\circ\text{C}$  and the resulting solution diluted with 157 ml anhydrous heptane. Then 31.5 ml polymethylhydroxyloxane was added ( $d=0.99\text{ g/ml}$ ,  $M_w=2256$ ). After allowing the solvents to settle and siphoning off the supernatant, the solid was washed 3 times with 150 ml portions of anhydrous heptane.

At  $50^\circ\text{C}$ , 18.4 ml of  $\text{SiCl}_4$  was added over a 15 minutes period, then treated with 2.7 ml 2,2-diisobutyl-1,3-dimethoxypropane and maintained at  $50^\circ\text{C}$  for 2 hours. The solids were allowed to settle and the supernatant removed by siphon and washed 4 times with 120 ml portions of anhydrous hexane. The residue was treated with 52.3 ml of  $\text{TiCl}_4$  and then heated at  $90^\circ\text{C}$  for 2 hours. The liquid was removed by siphon after the solids were allowed to settle, the solid residue was washed repeatedly with anhydrous heptane at  $60^\circ\text{C}$  and then 5 times at room temperature, until there were no chlorine ions in the wash liquid. After vacuum drying, the solid catalyst component contained 1.65% Ti and 14.9% 2,2-diisobutyl-1,3-dimethoxypropane.

Propylene was polymerized according to procedure B.2 using 0.57 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  and 0.4 ml hexane suspension containing 7.9 mg solid catalyst component. 229 g of polymer was obtained with a polymer yield of 29 kg per g; of catalyst component 96.2% insoluble residue in xylene at  $25^\circ\text{C}$  and a tamped bulk density 10 AD of 0.42 g/cc.

Example 7

Into a 1 l glass flask equipped with condenser, mechanical agitator and thermometer, under anhydrous nitrogen atmosphere, was introduced 572 ml solution containing 11.4 g  $\text{Al}(\text{C}_2\text{H}_5)_3$  for each 100 ml hexane. While agitating at  $5^\circ\text{C}$ , 40 g spherical  $\text{MgCl}_2 \cdot 2.6\text{C}_2\text{H}_5\text{OH}$  support, prepared according to method of example 1 in U.S. patent No. 4,469,648 was added over 90 minutes, then heated to  $60^\circ\text{C}$  for 3.5 hours, the solids were allowed to settle and the supernatant removed by siphon. The solid residue was washed 10 times with 200 ml portions of anhydrous heptane.

To the product obtained, which was diluted to 100 ml with anhydrous heptane, was added over 2 hours at  $80^\circ\text{C}$ , 2.7 ml  $n\text{-C}_4\text{H}_9\text{OH}$  diluted with 1.5 ml anhydrous heptane. The solid were allowed to settle and the liquid siphoned off. The solid was washed repeatedly with 150 ml portions anhydrous hexane. After vacuum drying the solid showed a Mg content of 20.9% and  $\text{C}_2\text{H}_5\text{OH}$  of 3.6%.

In a 500 ml glass flask was introduced, under an anhydrous nitrogen environment, 362 ml  $\text{TiCl}_4$ , then while agitating at  $0^\circ\text{C}$ , 14.5 g of the solid catalyst component obtained above were added. Over a 1 hour period the contents were heated to  $100^\circ\text{C}$ . When the temperature reached  $40^\circ\text{C}$ , 4.8 ml 2,2-diisobutyl-1,3-dimethoxypropane was added. The contents were heated at  $100^\circ\text{C}$  for 2 hours. The solids allowed to settle and the liquid was siphoned off.

To the solid residue 319 ml of  $\text{TiCl}_4$  was added, heated to  $120^\circ\text{C}$  for 1 hour, and then the liquid was removed by siphoning after settling. The solid was washed repeatedly with 150 ml portions anhydrous hexane first at  $60^\circ\text{C}$  and then at room temperature. After vacuum drying the catalytic solid contains 2.45% Ti and 6.3% 2,2-diisobutyl-1,3-dimethoxypropane.

Propylene was polymerized according to procedure A.1 using 0.76 g  $\text{Al}(\text{C}_2\text{H}_5)_3$ , 0.09 ml hexane solution containing 8.9 mg solid catalyst component and 1000 ml hydrogen. 430 g of polymer was obtained with a polymer yield of 51.8 Kg/g catalyst component, 90.4% insoluble residue in xylene at  $25^\circ\text{C}$ , a melt index of 8.9 g/10' and a tamped bulk density of 0.49 g/ml.

Examples 8-18 and comparative examples 1-3

Into a 500 ml reactor equipped with filtering disk 225 ml  $\text{TiCl}_4$  was introduced at  $0^\circ\text{C}$ . While agitating 10.1 g (54 mmoles) microspheroidal  $\text{MgCl}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$ , obtained according to the method of example 1 of U.S. patent 4,469,648, was added. Upon completing the addition, the temperature was brought to  $40^\circ\text{C}$  and 9 mmoles ether was introduced. The temperature was raised to  $100^\circ\text{C}$  over one hour period and allowed to react for 2 hours after which the unreacted  $\text{TiCl}_4$  was removed by filtration. Another 200 ml  $\text{TiCl}_4$  was added and allowed to react at  $120^\circ\text{C}$  for 1 hour, filtered and washed with n-heptane at  $60^\circ\text{C}$  until the chlorine ions disappeared from the filtrate.

The ethers used and the analytical data relative to the solid catalyst component obtained in this manner

are reported in table 2.

Examples 19-36 and comparative examples 4-6

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The polymerization data with the catalysts obtained from the solid catalyst components prepared according to examples 8-18 and comparative examples 1-3 are reported in table 3.

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Table 2

Ex. No.	Ether used	Composition of the solid catalyst component % by weight		
		Mg	Ti	Ether
=====				
8	2,2-dimethyl- 1,3-dimethoxypropane		2.6	10.40
9	2-isopropyl-2-methyl- 1,3-dimethoxypropane	21.7	3.24	10.44
10	2,2-diisobutyl- 1,3-dimethoxypropane	16.64	3.1	15.5
11	2,2-diisobutyl- 1,3-diethoxypropane		4.3	8.10
12	2,2-diisobutyl- 1,3-di-n-butoxypropane	16.3	5.2	2.40
13	2,2-diphenyl- 1,3-dimethoxypropane	14.5	5.59	11.10
14	2,2-bis (cyclohexylmethyl) 1,3-dimethoxypropane	14.87	4.43	11.4
15	1,3-diisobutoxypropane		4.7	0.005
16	2,2-pentamethylene 1,3-dimethoxypropane		2.9	15.1
17	1,1-bis (methoxymethyl) bicyclo- (2,2,1)-heptane		3.3	11.7
18	2-isopentyl-2-isopropyl- 1,3-dimethoxypropane		2.5	14.8

Table 2 (follow)

5	Comp. 1	1,3 dimethoxypropane	18.0	1.7	10.6
10	Comp. 2	1-isopropyl-2,2-dimethyl 1,3-dimethoxypropane	17.0	4.3	0
15	Comp. 3	1,1-dimethoxyethane	20.8	3.0	4.0

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Table 3

Ex. No.	Catalyst Com- ponent Ex.No.	Polymer Yield g polymer/gCat. comp.	I.I. %	dl/g	Polymerization Method
19	8	3100	89.8	2.15	B.2.1.
20	9	8700	93.3	2.90	B.2.1.
21	10	9300	95.3		B.2.1.
22	11	14200	79.7		B.2.1.
23	12	13600	84.3	2.10	B.2.1.
24	13	9100	84.8	2.48	B.2.1.
25	14	19000	88.4	1.65	B.2.1.
26	15	20100	75.0		B.2.1.
27	16	7100	89.3		B.2.1.
28	17	8500	79.8		B.2.1.
29	18	11000	98.0		B.2.1.
Comp. 4	Comp. 1	1800	64.9		B.2.1.
Comp. 5	Comp. 2	2000	72.0	1.0	B.2.1.
Comp. 6	Comp. 3	4300	68.1	1.77	B.2.1.
30	10	8900	96.1	2.39	B.2.2.
(dimethyl dimethoxysilane)					
31	10	7900	96.3	2.00	B.2.2.
(2,2-diisobutyl-1,3-dimethoxypropane)					

Table 3 (follow)

5	32	10	5100	97.5	2.15	B.2.2.
	(phenyltriethoxysilane)					
	33	10	33400	92.0	1.56	A.1.
10	(2,2-diisobutyl-1,3-dimethoxypropane)					
	34	10	23200	96.0	1.71	A.1.1.
15	35	10	36600	93.8	1.83	A.1.1.
	(2,2,6,6-tetramethylpiperidine)					
	36	10	9600	96.6	1.94	A.1.1.
20	(ethyl p.toluate)					

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## Example 37

30 A 1.4 stainless steel autoclave, equipped with a thermostat and mechanical agitator, was purged with gaseous propylene at room temperature for 1 hour. Then, while agitating, 66 g of butadiene, 230 g of liquid propylene and 300 ml of hydrogen were fed. Under propylene pressure a catalytic suspension of 0.6 Al-(Et)<sub>3</sub> TEAL and 0.048 g solid catalyst component of example 1. The temperature was rapidly brought to 70°C (in 5 min) and the resulting pressure was 24.6 atm. These conditions were maintained for 4 hours reintegrating feeding propylene continuously to reintegrate the portion polymerized. The autoclave was then  
 35 degassed and cooled at room temperature. 64 g polymer, dried in an oven under nitrogen at 60°C for 4 hours, was recovered, with a yield of 1333 g polymer per g catalyst. When analyzed, using standard methods, the polymer showed the following characteristics:  
 [η] in tetrahydronaphthalene at 135°C = 1.8 dl/g.

MIL = 4 g/10'

- 40 Soluble in xylene at 25°C = 24.1% (weight).  
 Butadiene content (determined via IR):  
 - raw polymer = 0.6% 1,2; 3.7% 1,4 trans  
 - insoluble in xylene = 0.5% 1,2; 1.6% 1,4 trans  
 - soluble in xylene = < 0.25% 1,2; 8.2 1,4 trans.

## Example 38

50 The autoclave and procedure of example 37 was used to polymerize propylene with the solid catalyst component of example 1, but using instead of Al-triethyl, a mixture of 3.3 mmoles Al-triethyl and 3.3 mmoles Al-diethylmonochloride and 0.018 g solid catalyst component.

380 g of a polymer with a polymer yield of 35.2 kg/g of catalyst component, a 94.1% insoluble residue in xylene at 25°C, and a melt index of 7.3 g/10'.

## Example 39

In the same autoclave used in example 1 was charged at 30°C and without agitation, a catalyst



suspension of 0.9 g Al-triethyl and 0.09 g of the solid catalyst component of example 37 in about 18 ml hexane. Then 800 g propane was introduced with agitation. The temperature was rapidly brought to 75 °C, and then 2 atm hydrogen, 200 g butene-1 were introduced. Ethylene was then introduced until the pressure reached 33 atm. These conditions were maintained for 2 hours maintaining constant pressure by continuously feeding with a mixture of ethylene and butene-1 in a weight ratio of 10/1. The autoclave was degassed and cooled at room temperature.

The amount of polymer, obtained after drying at 70 °C under nitrogen for 4 hours, was 280 g, which corresponded to a yield of 31.1 kg per g of catalyst component.

Analyzed using standard methods, the product showed the following characteristics:

- MIE = 0.23 g/10' (F/E = 26.7)
- MIF = 6.16 g/10'
- Butene (determined via IR) = 6% (weight)
- Density = 0.9211 g/cm<sup>3</sup>
- Soluble in xylene at 25 °C = 6.3% (weight)

#### Example 40

In the same autoclave used in example 3 purged as described therein but using ethylene instead of propylene, was introduced at 45 °C under hydrogen flow, a 900 ml solution of 0.5 g/l of Al-triisobutyl in anhydrous hexane and immediately after 0.015 g of solid catalyst component of example 1 suspended in 100 ml of the above mentioned solution. The contents were rapidly heated to a temperature of 75 °C, then hydrogen was fed until the pressure reached 4.5 atm. These conditions were maintained for 3 hours continuously replacing the ethylene polymerized. The autoclave was rapidly degassed and cooled at room temperature. The polymeric suspension was filtered and the solid was dried at 60 °C under nitrogen for 8 hours.

300 g of polymer was obtained (corresponding to a yield of 20 kg/g of catalyst component) which had the following characteristics (determined by standard methods):

- MIE = 1.74 g/10' (MIF/MIE = 26.5)
- MIF = 48 g/10'
- $[\eta]$  135 °C THN = 1.78 dl/g
- tamped bulk density = 0.362 g/ml

Other features, advantages and embodiments of the invention disclosed herein will be readily apparent to those exercising ordinary skill after reading the foregoing disclosures. In this regard, while specific embodiments of the invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

#### Examples 41-51

Catalyst components are prepared according to the procedure of examples 8-18 by using different ethers. The ethers used and the analytical data relative to the solid catalyst component obtained in this matter are reported in Table 4.

#### Examples 52-62

The polymerization data with the catalyst obtained from the solid catalyst components prepared according to examples 41-51 are reported in Table 5.

Table 4

Ex. No.	Ether used	Composition of the solid catalyst component % by weight		
		Mg	Ti	Ether
41	2-isopropyl-2- 3,7 dimethyloctyl-1,3- dimethoxypropane	13.4	3.3	17.6
42	2,2-diisopropyl-1,3- dimethoxypropane	16.1	3.2	13.8
43	2-isopropyl-2- cyclohexylmethyl-1,3- dimethoxypropane	14.3	3.7	14.5
44	2,2-dicyclohexyl-1,3- dimethoxypropane	16.0	4.5	15.3
45	2-isopropyl-2-isobutyl-1,3- dimethoxypropane	16.0	3.6	14.5
46	2,2-diisopentyl-1,3- dimethoxypropane	15.1	3.1	11.3
47	2,2-dipropyl-1,3- dimethoxypropane	14.3	2.1	18.3
48	2-isopropyl-2-cyclohexyl- 1,3-dimethoxypropane	16.1	3.2	14.8
49	2-isopropyl-2-cyclopentyl- 1,3-dimethoxypropane	15.0	2.6	13.4
50	2,2-dicyclopentyl-1,3- dimethoxypropane	15.5	3.4	16.2
51	2-heptyl-2-pentyl-1,3- dimethoxypropane	14.4	4.6	16.0

Table 5

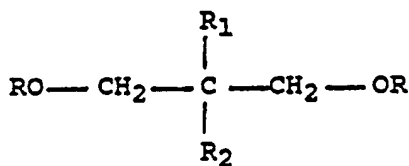
Ex. No.	Catalyst Ex.No.	Polymer yield g polymer/gCat. comp.	I.I %	$\{\eta\}$ dl/g	Polymerization Method
52	41	12190	91.5	1.85	B.2.1.
53	42	10750	95.9	1.88	B.2.1.
54	43	8410	94.2	1.76	B.2.1.
55	44	22900	95.7	2.27	B.2.1.
56	45	16000	95.5	2.32	B.2.1.
57	46	18900	96	1.48	B.2.1.
58	47	13000	94.6	1.74	B.2.1.
59	48	22200	95	1.72	B.2.1.
60	49	19000	96.2	1.66	B.2.1.
61	50	12000	95.5	1.90	B.2.1.
62	51	20600	88	1.72	B.2.1.

## Claims

1. A solid catalyst component for the polymerization of olefins comprising a magnesium dihalide in active form and supported thereon a titanium compound containing at least one Ti-halogen bond and an electron-donor compound selected from ethers containing two or more ether groups and further characterized by the formation of complexes with anhydrous magnesium dichloride at less than 60 mmoles per 100 g of magnesium chloride and the failure to enter into substitution reactions with  $\text{TiCl}_4$  or of reacting that way at less than 50% by moles.

2. The solid catalyst component of claim 1 where the ethers are characterized by the formation of complexes with anhydrous magnesium dichloride in quantities between 20 and 50 mmoles per 100 g of magnesium dichloride.

3. The solid catalyst component of claim 1 wherein the ethers are selected from diethers with the following general formula:



where R,  $\text{R}_1$  and  $\text{R}_2$ , independently, are linear or branched alkyl, cycloaliphatic, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms and  $\text{R}_1$  or  $\text{R}_2$  may also be hydrogen.

4. The solid catalyst component of claim 3 wherein R is methyl, and when  $\text{R}_1$  is methyl, ethyl, propyl or isopropyl,  $\text{R}_2$  is ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, 2-ethylhexyl, cyclohexyl, methylcyclohexyl, phenyl or benzyl, and when  $\text{R}_1$  and  $\text{R}_2$  are the same, they are ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, neopentyl, isopentyl, phenyl, benzyl, cyclopentyl or cyclohexyl.

5. The solid catalyst component of claim 3 wherein R is methyl and  $\text{R}_1$  and  $\text{R}_2$  are different and are isopropyl, isobutyl, t-butyl, cyclohexyl, isopentyl or cyclohexylethyl.

6. The solid catalyst component of claim 3 where the ethers are 2,2-diisobutyl-1,3-dimethoxypropane, 2-

isopropyl-2-isopentyl-1,3-dimethoxypropane, 2,2-bis(cyclohexyl-methyl)-1,3-dimethoxypropane, 2-isopropyl-2-3,7-dimethyloctyl-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-methyl-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-isobutyl-1,3-dimethoxypropane, 2,2-diisopentyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2-heptyl-2-pentyl-1,3-dimethoxypropane.

7. The solid catalyst component of one or more of the preceding claims wherein the titanium compound is selected from the group consisting of the halo alcoholates and the halides of titanium and the magnesium dihalide is magnesium dichloride.

8. The solid catalytic component of claim 7 wherein the titanium compound is titanium tetrachloride.

9. The solid catalytic component of claim 7 wherein the magnesium dichloride is present in active form characterized in that in the X-ray powder spectrum of the catalyst component a halo appears instead of the most intense diffraction line which appears at an interplanar distance of 2.56 Å in the non-activated magnesium dichloride and the maximum intensity of the halo is shifted with respect to said interplanar distance.

10. The solid catalyst component of one or more of the preceding claims wherein the ether is present in an amount from 5 and 20% mmols with respect to the magnesium dihalide.

11. The solid catalyst component of one or more of the preceding claims wherein the Mg/Ti ratio is between 30:1 and 4:1.

12. The solid catalyst component of one or more of the preceding claims wherein the magnesium dichloride in active form is obtained from MgCl<sub>2</sub> complexes with alcohols or titanium alcoholates, or from alcoholates and chloroalcoholates of magnesium.

13. The solid catalyst component of one or more of the preceding claims wherein the magnesium dichloride and the titanium compound are supported on resins and the Mg/Ti ratio is from 2:1 to 3:1.

14. A catalyst for the polymerization of olefins CH<sub>2</sub>=CHR, wherein R is H, an alkyl radical with 1-6 carbon atoms or an aryl, or mixtures thereof with or without a diolefin, comprising the product obtained by reaction of a solid catalyst component of claim 3 with an Al-alkyl compound.

15. The catalyst of claim 14 wherein the Al-alkyl compound is an Al-trialkyl.

16. The catalyst of claim 15 for the polymerization of olefins CH<sub>2</sub>=CHR wherein R is an alkyl radical with 1-6 carbon atoms, further comprising, in addition to the Al-trialkyl compound 2,2,6,6-tetramethylpiperidine or a silicon electron donor compound containing at least one Si-OR bond wherein R is a hydrocarbon radical.

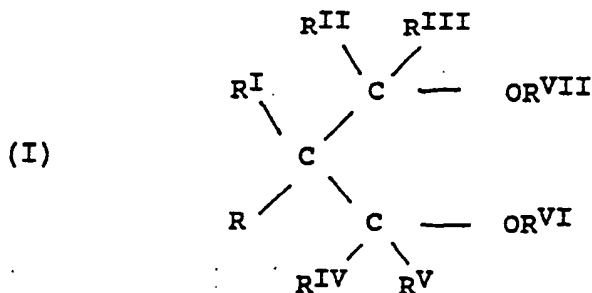


## DESCRIPTION

The present invention refers to a new class of diethers.

The diethers of the invention are useful as additives for fuels (where they produce an increase in the octane number), as solvents, as a complexing agent for metal ions, and in the preparation of Ziegler-Natta catalysts.

The diethers have the general formula:



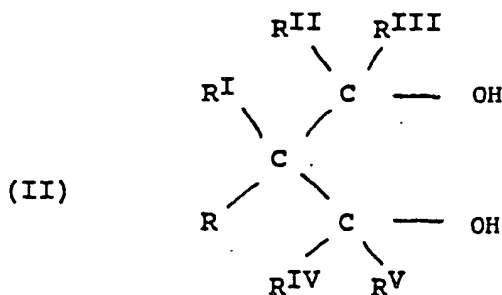
where R, R<sup>I</sup>, R<sup>II</sup>, R<sup>III</sup>, R<sup>IV</sup> and R<sup>V</sup>, same or different, are H or linear or branched alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, provided that R and R<sup>I</sup> are not both H or CH<sub>3</sub> or are not CH<sub>3</sub> and n-propyl; R<sup>VI</sup> and R<sup>VII</sup>, the same or different, are linear or branched alkyl, cycloalkyl, aryl, alkylaryl



radicals with 1-18 carbon atoms; one or more of R to R<sup>VII</sup> can be bonded to form a cyclic structure.

Preferably R<sup>VI</sup> and R<sup>VII</sup> are alkyl radicals with 1-6 carbon atoms, R<sup>II</sup>, R<sup>III</sup>, R<sup>IV</sup> and R<sup>V</sup> are hydrogen. When R and R<sup>I</sup> are alkyl radicals, they have preferably 3 or more carbon atoms.

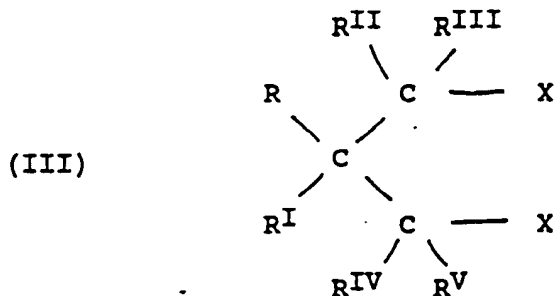
The new diethers may be prepared according to various methods. For example, they may be prepared according to known etherification reactions such as the ones listed below, starting from the corresponding diols of general formula (II)



- 1) Reaction of diols of formula II or the corresponding alkaline alcoholates with compounds of formula R<sup>VI</sup>-X, R<sup>VII</sup>-X or their mixtures (where X = Cl, Br, I, C<sub>6</sub>H<sub>5</sub>-SO<sub>3</sub>, p-CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>, CH<sub>3</sub>SO<sub>3</sub>), wherein R, R<sup>I</sup>, R<sup>II</sup>, R<sup>III</sup>, R<sup>IV</sup> and R<sup>V</sup> have the same meaning as set forth above.
- 2) Reaction of diols of formula II with dialkyl sulfates of formula R<sub>2</sub><sup>VI</sup> SO<sub>4</sub> or R<sub>2</sub><sup>VII</sup> SO<sub>4</sub> in alkaline environment.
- 3) Reaction of derivatives of general formula III, using



known techniques, starting from the diols of formula II



(wherein R to R<sup>V</sup> and X have the meaning as indicated above) with R<sup>VI</sup>-OM and R<sup>VII</sup> OM alcoholates, wherein M = Na, K, Mg, Ca or mixtures thereof.

- 4) Thermal or catalytic dehydration of mixtures of diols of general formula (II) with R<sup>VI</sup> OH or R<sup>VII</sup> OH alcohols or mixtures thereof.

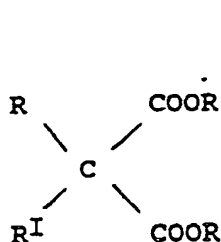
These and other suitable methodologies are described in:

- 1) Houben Weil - Methoden der Organischen Chemie Vol VI/3 Verlag ed. Stuttgart 1965.
- 2) G.W.Gokel and Coll. Synthesis 1976, 168.
- 3) G. Johns and Coll. ibid. 1976, 515.
- 4) D. Achet and Coll. ibid. 1986, 642.

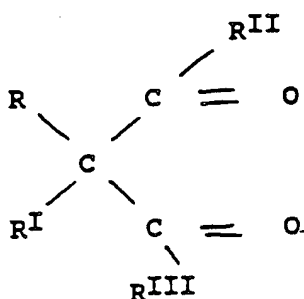
The diols of general formula (II) may in turn be synthesized, for example, according to known methods such



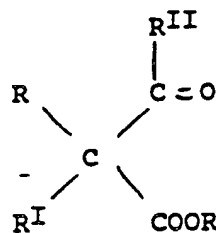
as the reduction of the corresponding diesters, dialdehydes, diketones, ketoaldehydes or dicarboxylic acids, having the general formula IV and V, and ketoesters and aldehyde esters of general formula (VI)



(IV)



(V)



(VI)

(where the radicals R, RI, RII, RIII have the meaning as indicated above).

Examples of these methods are described in:

- H. Adkins, Organic Reactions 8, 1 (1954)
- N.G. Gaylord, Reduction with Complex Metal Hydrides, Interscience Publishers, N.Y., London 1956.
- R. F. Nystrom, W. G. Brown, J. Am. Chem. Soc. 69, 1197 (1947).

Furthermore diols of formula II (wherein RII, RIII, RIV, and RV are H) may also be prepared from aldehydes of general



formula VII



wherein R and R' have the same meaning as already specified, by action of alkaline formaldehyde according to the Cannizzaro reaction (see for example Organic Reactions Vol II, pag. 94 -J. While ed. - N.Y., 1944).

Diols of general formula II may easily be converted into the corresponding III derivatives by known methods (see Houben Weil, Methoden der organischen Chemie, Band V/3, V/4, IX; Verlag ed. Stuttgart).

The following examples illustrate the following ethers of the invention and methods of preparing same:

- 2-methyl,2-isopropyl-1,3-dimethoxypropane
- 2,2-diisobutyl-1,3-dimethoxypropane
- 2,2-diphenyl-1,3-dimethoxypropane
- 2,2-dibenzyl-1,3-dimethoxypropane
- 2,2-bis(cyclohexylmethyl)1,3-dimethoxypropane
- 2,2-diisobutyl-1,3-dibutoxypropane
- 2,2-diisobutyl-1,3-ethoxypropane
- 2-isopentyl,2-isopropyl-1,3-dimethoxypropane



- 2,2,4-trimethyl-1,3-dimethoxypentane
- 1,1'-bismethoxymethylcyclohexane
- (+/-) 2,2'-bis(methoxymethyl)norbornane (racemic mixture).

Other examples of ethers are:

- 2-isopropyl-2-3,7-dimethyloctyl-1,3-dimethoxypropane
- 2,2-diisopropyl-1,3-dimethoxypropane
- 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane
- 2,2-diisopentyl-1,3-dimethoxypropane
- 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane -
- 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane
- 2,2-dicyclopentyl-1,3-dimethoxypropane
- 2-heptyl-2-pentyl-1,3-dimethoxypropane
- 2,2-dicyclohexyl-1,3-dimethoxypropane
- 2-isopropyl-2-isobutyl-1,3-dimethoxypropane
- 2,2-dipropyl-1,3-dimethoxypropane.

#### Example 1

Preparation of 2,2-diisobutyl-1,3-dimethoxypropane.

##### a) Preparation of diisobutyl ethyl malonate.

Into a 250 ml flask, equipped with an agitator, refrigerant, charge funnel, thermometer and tube for the introduction of gases, were charged, under nitrogen flow, 100 g anhydrous ethanol and 5 g (0.22 moles) Na.

When the dissolution of Na was complete, 16 g (0.1 moles) diethylmalonate was introduced, and stirred at room temperature for a few minutes. Then 28 g isobutyl bromide



(0.21 moles) was added and the mixture was refluxed with agitation for 6 hours. Subsequently, 7.5 g dry sodium ethylate (0.12 moles) and 14 g isobutyl bromide (0.1 moles) were added. The agitation and the reflux heating was continued for 8 more hours.

Most of the solvent was distilled off at reduced pressure (50 mm Hg), and the remainder was extracted with 200 ml hexane. The distilled hexane solution provided 15.5 g of diisobutyl ethylmalonate with a boiling point of 145-146°C/20 mm Hg. The product has a gas-chromatographic purity (main peak area) of 97.5%, and coincides with a sample of diisobutyl ethylmalonate prepared according to Bently and Perkin, J. Chem. Soc. 73, 61.

b) Preparation of 2,2-diisobutyl-1,3-propandiol.

Into the same apparatus as described above in a) were introduced, under nitrogen flow, 100 ml diethyl ether and 3 g  $\text{LiAlH}_4$  (0.079 moles).

Then dropwise over a period of one hour while maintaining vigorous agitation, 15.5 g diisobutyl ethyl malonate from a) above was added and the mixture refluxed for 30 minutes.

The reaction mixture was then poured into a vessel containing 100 g ice acidified with dil. HCl and extracted with 3 portions of 100 ml of ethyl ether.

The ether was evaporated and 10 g of a raw material was produced which, when crystallized from hexane, gave 8.5 g of 2,2-diisobutyl-1,3-propandiol with melting point 75-77°C and an elemental analysis of C=70.3% and H=12.6%.

The theoretical value for  $C_{11}H_{24}O_2$  is C=70.21% H=12.7%.

c) Preparation of 2,2-diisobutyl-1,3-dimethoxypropane.

Into the same apparatus as described above in a) was introduced, under nitrogen, 8.5 g (0.06 moles) 2,2-diisobutyl-1,3-propandiol, 200 ml dioxane and 15.4 g (0.136 moles) potassium tert-butyrate.

The mixture was stirred at room temperature for 30 minutes and then 20 g  $CH_3I$  (0.14 moles) was added dropwise. During this procedure, the temperature rises spontaneously to 50°C.

After 2 hours, an additional quantity of potassium tert-butyrate (154 g, 0.136 moles) and of  $CH_3I$  (20 g, 0.14 moles) was added, and the mixture refluxed for 1 hour.

The reaction mass was filtered and the filtrate distilled at reduced pressure. Among other products, 7.4 g of 2,2-diisobutyl-1,3-dimethoxypropane having a boiling point 100-101°C/22 mm-Hg which by gas layer chromatography (GLC) shows a purity of 99% (chromatographic peaks area) was obtained.

$n_D^{20} = 1.4337$ .

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS as internal standard):

signals at 0.89 ppm, doublet 12 H

1.21 ppm, doublet 4 H

1.68 ppm, multiplet 2 H

3.16 ppm, singlet 4 H

3.26 ppm, singlet 6 H

Using the procedures of a), b) and c) above the following compounds were obtained:

1) 2-methyl-2-isopropyl-1,3-dimethoxypropane

$n_{D_{20}} = 1.4209$ , boiling point 160°C-161°C/760 mmHg

2) 2,2-dibenzyl-1,3-dimethoxypropane

p.f. 105°C (from petroleum ether)

3) 2,2-diisobutyl-1,3-dibutoxypropane

$n_{D_{20}} = 1.4378$ , boiling point 115°C-117°C/1 mmHg

4) 2,2-diisobutyl-1,3-diethoxypropane

$n_{D_{20}} = 1.4302$ , boiling point 118°C-120°C/20 mmHg

#### Example 2

Preparation of 2,2-bis(cyclohexymethyl)-1,3-dimethoxypropane.

Into a stainless steel autoclave provided with an anchor agitation system, 5.8 g (0.02 moles) of  $(C_6H_5CH_2)_2C(CH_2OCH_3)_2$  prepared according to example 1, 100 ml n-hexane and 10 g Raney Ni washed by decanting with 3 parts 50 cc anhydrous ethanol and subsequently with 3 parts 50 cc of hexane, were introduced.



The autoclave was pressurized with 17 atm. of hydrogen and was heated to 135°C (internal temperature) for 8 hours with agitation.

After cooling, the reaction mixture, was filtered from the catalyst and vacuum evaporated, to yield 5.9 g of a colorless oil with a purity of 99%  $n_{D_{20}}^{20} = 1.4790$ . The only compound detectable by thin layer chromatography (TLC), was 2,2-bis(cyclohexyl,methyl)-1,3-dimethoxypropane.

$^1\text{H}$ NMR(300 MHz,  $\text{CDCl}_3$ , TMS as internal standard).

Signals at:

0.96 ppm multiplet 4 H

1.18 ppm multiplet 12 H

1.63 ppm multiplet 10 H

3.15 ppm singlet 4 H

3.27 ppm singlet 6 H

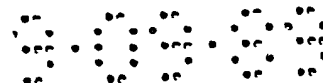
### Example 3

Preparation of 2,2-diphenyl-1,3-dimethoxypropane.

a) Preparation of 2,2-diphenyl-1,3-propandiol.

Into the same apparatus described in example 1 (a)), 10.6 g (0.054 moles) of  $(\text{C}_6\text{H}_5)_2\text{CHCHO}$  (Fluka), 4.03 g (0.028 moles)  $\text{K}_2\text{CO}_3$ , 10 cc water, 13.2 ml aqueous formaldehyde at 40% (0.176 moles) and 35 ml ethanol at 99% purity were introduced.

The mixture was stirred and refluxed for 6 hours, cooled



and diluted with 200 ml of water. The precipitate thus formed was filtered, washed with water and crystallized from benzene to give 9.6 g of 2,2-diphenyl-1,3-propandiol with a m.p. 102-104°C.

b) Preparation of 2,2-diphenyl-1,3-dimethoxypropane.

Into the same apparatus as described in a) was charged 9.6 g 2,2-diphenyl-1,3-propandiol dissolved in 400 ml anhydrous tetrahydrofuran and stirred under nitrogen with 3.8 g NaH (55% NaH dispersed in vaseline oil) until the production of hydrogen stops. Over a period of 20 minutes, 9.6 ml  $\text{CH}_3\text{I}$  was added and stirring continuously for 2 hours. Most of THF was distilled off; then the product is diluted with water (200 ml) and extracted with two 50 ml portions of diethyl ether. The ether extract gives, by vacuum distillation, 3.5 g of 2,2-diphenyl-1,3-dimethoxypropane having boiling point of 188°C-190°C/20 mm Hg which was unitary by TLC-chromatography and having  $n_{\text{D}20}^{\text{D}} = 1.5558$ .

According to the same procedure described above in a) and b) the following compounds were prepared starting respectively from hexahydrobenzenaldehyde and norbornan-2-carboxaldehyde.



## A) 1,1-dimethoxymethylcyclohexane

boiling point  $97^{\circ}$ - $98^{\circ}\text{C}/20$  mm Hg;  $n_{\text{D}20}^{\text{D}} = 1.4487$

$^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ , TMS as internal standard):

signals at:

1.36 ppm multiplet 10 H

3.20 ppm singlet 4 H

3.29 ppm singlet 6 H

## B) (+/-) 2,2-dimethoxymethylnorbornane

boiling point  $106^{\circ}$ - $108^{\circ}\text{C}/20$  mm Hg;  $n_{\text{D}20}^{\text{D}} = 1.4659$

$^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ , TMS as internal standard)

Signals at:

0.72 ppm doublet 1 H

1.14 ppm doublet 1 H

1.06 ppm multiplet 1 H

1.34 ppm multiplet 2 H

1.51 ppm multiplet 3 H

1.97 ppm singlet (broad) 1 H

2.15 ppm singlet (broad) 1 H

3.06 ppm system AB 1 H

3.14 ppm system AB 1 H

3.33 ppm system AB 1 H

3.36 ppm system AB 1 H





3.29 ppm multiplet 6 H

Example 4

Preparation of 2,2,4-trimethyl-1,3-dimethoxypentane.

Into a 2 l flask provided with an agitator, refrigerant, charge funnel, thermometer and tube for the introduction of gases, are charged, under nitrogen flow:

29.2 g (0.2 moles) 2,2,4-trimethyl-1,3-propandiol, 600 ml dioxane, and 10 g (0.2 moles) NaH at 50% concentration in vaseline oil. The contents were agitated until the production of gas ceased; then heated to 80°C, and 18 ml CH<sub>3</sub>I (0.28 moles) was introduced dropwise. After two hours 10 g NaH at 50% concentration (0.2 moles) in vaseline oil and 40 cc CH<sub>3</sub>I (0.62 moles) were added.

After reflux heating for 8 hours the reaction mixture was diluted with 1.5 l of water and extracted with 3 portions of hexane (100 ml each).

The extract was washed with water and dried, and on vacuum distillation, gave 22.5 g of 2,2,4-trimethyl-1,3-dimethoxypropane having a boiling point 105°C/70 mm Hg whose purity (peak areas) is 98.6% by GLC and

$n_{D20}^D = 1.4227$

<sup>1</sup>HNMR (60 MHz, CDCl<sub>3</sub>, TMS as internal standard)



signals at:

1.5 ppm multiplet 12 H

3.7 ppm multiplet 3 H

4.1 ppm multiplet 6 H

Example 5

Preparation of 2-isopentyl-2-isopropyl-1,3-dimethoxypropane.

a) Isopentylidenisopentanal preparation.

50 g isopentanal are reacted according to the procedures described in DRP 643341 (1933 I.G. Farb.) and DRP 544192 (1933 I.G. Farb.).

27 g of 2-isopentylideneisopentanal, having a boiling point 98-102°C/20 mm Hg are obtained.

b) Preparation of 2-isopentylisopentanal.

Following the hydrogenation method described by J. V. Braun and G. Manz, Ber. 1969, 67 (1934) starting from 27 g 2-isopentylideneisopentanal, 27 g of raw material was obtained which was not characterized. The hydrogen absorption measured was consistent with the reaction reported.

c) Preparation of 2-isopropyl-2-isopentyl-1,3-propandiol.

Into the same apparatus of example 1 a) 27 g raw aldehyde from the preceding preparation for b), 16 g K<sub>2</sub>CO<sub>3</sub>, 200 ml



99% pure ethanol and 52 ml aqueous  $\text{CH}_2\text{O}$  at 40% concentration were introduced, and maintained at reflux with agitation for 4 hours. Then the reaction mixture was diluted with 1 l water, extracted with two 250 ml portions of ether. The ether was evaporated and the ether extract dried and distilled at reduced pressure providing (among other compounds) 9 g of 2-isopropyl-2-isopentyl-1,3-propandiol having a boiling point of  $165^\circ\text{C}/20$  mm Hg and being unitary by TLC. This material was used for the next reaction without further analysis.

d) Preparation of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane.

Into the apparatus of example 1 a) under nitrogen flow, 9 g of raw material from c) above, 200 cc dioxane, and 15 g  $(\text{CH}_3)_3\text{COK}$  (potassium terbutylate) were charged and agitated for about 30 minutes. Then 10 ml  $\text{CH}_3\text{I}$  was introduced over a period of one hour, and the contents refluxed for 5 hours. The reaction mixture was diluted with 1 l water and extracted with diethyl ether. The ether was evaporated and the ether extract dried and distilled at reduced pressure. Among other compounds, 7.3 g of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane having a



boiling point of 130-133°C/35 mm Hg and a gas-chromatographic purity of 98.6% (peak areas).

$n_{D_{20}} = 1.4365$

$^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ , TMS as internal standard)

signals at:

0.87 ppm doublet 6 H

8.89 ppm doublet 6 H

1.11 ppm multiplet 2 H

1.28 ppm multiplet 2 H

1.42 ppm multiplet 1 H

1.76 ppm multiplet 1 H

3.23 ppm singlet 2 H

3.24 ppm singlet 2 H

#### Example 6

In a 500 ml flask was introduced, under agitation, 60 ml n-heptane and 67 ml tetra-n-butoxy-titanium, and heated to 45°C. Over a period of three hours, a solution of  $\text{Al Et}_2\text{Cl}$  (44.8 ml) in n-heptane (108 ml) was gradually introduced.

The temperature was raised to 60°C for one hour and then cooled to room temperature.

A solid was separated and washed four times with 100 ml portions heptane and then vacuum dried.



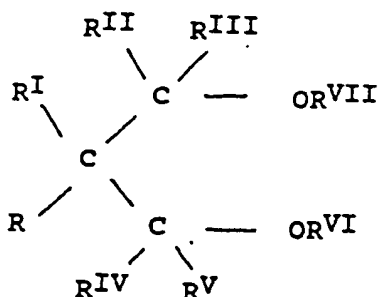
Into a flask, 8.1 g of this solid was introduced together with 20.3 m moles titanium tetrachloride, 20.3 ml toluene, and 20.3 m moles 2,2-diisobutyl-1,3-dimethoxypropane and heated to 60°C for one hour, and then at 100°C for 4 hours. The reaction mixture was then cooled at room temperature, the solid product was separated, washed with n-heptane until no chlorine ions were in the filtrate and dried in an oven under nitrogen flow.

In a 120 ml autoclave equipped with a magnetic agitator are introduced, after drying under nitrogen flow, 250 mg Al Et<sub>2</sub>Cl, 12.4 mg of the solid prepared above, and 80 ml liquid propylene, and heated to 60°C and maintained at this temperature for one hour under agitation. The excess unreacted propylene was discharged and 16.9 g of polypropylene was obtained with an isotactic index of 96.8% (extraction with n-heptane boiling for 4 hours).



# CLAIMS

## 1. Diethers of formula:



where R and R<sup>I</sup>, R<sup>II</sup>, R<sup>III</sup>, R<sup>IV</sup> and R<sup>V</sup> same or different, are H or linear or branched alkyl, cycloalkyl, aryl, alkyaryl or arylalkyl radicals with 1-18 carbon atoms, provided that R and R<sup>I</sup> are not both H or CH<sub>3</sub> or are not CH<sub>3</sub> and n-propyl; R<sup>VI</sup> and R<sup>VII</sup> are the same or different and are linear or branched alkyl, cycloalkyl, aryl, alkylaryl radicals with 1-18 carbon atoms; one or more of R to R<sup>VII</sup> can be bonded to form a cyclic structure.

2. Diethers according to claim 1 wherein R<sup>VI</sup> and R<sup>VII</sup> are alkyl radicals with 1-6 carbon atoms, R<sup>II</sup>, R<sup>III</sup>, R<sup>IV</sup> and R<sup>V</sup> are hydrogen, and when R and R<sup>I</sup> are alkyl radicals, they have 3 or more carbon atoms.



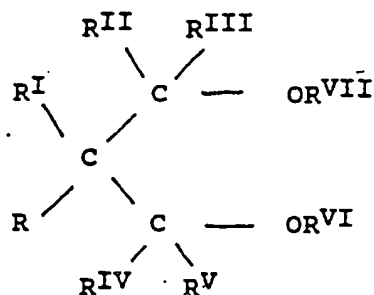
3. Diethers according to claim 2 selected from the group consisting of:

- 2,2-diisobutyl-1,3-dimethoxypropane
- 2,2-diphenyl-1,3-dimethoxypropane
- 2,2-dibenzyl-1,3-dimethoxypropane
- 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane
- 2-isopentyl-2-isopropyl-1,3-dimethoxypropane
- 2-isopropyl-2-3,7-dimethyloctyl-1,3-dimethoxypropane
- 2,2-diisopropyl-1,3-dimethoxypropane
- 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane
- 2,2-diisopentyl-1,3-dimethoxypropane
- 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane
- 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane
- 2,2-dicyclopentyl-1,3-dimethoxypropane
- 2-heptyl-2-pentyl-1,3-dimethoxypropane
- 2,2-dicyclohexyl-1,3-dimethoxypropane
- 2-isopropyl-2-isobutyl-1,3-dimethoxypropane
- 2,2-dipropyl-1,3-dimethoxypropane

# DIETHERS USABLE IN THE PREPARATION OF ZIEGLER-NATTA CATALYSTS

## ABSTRACT

Diethers of general formula:



where R, R<sup>I</sup>, R<sup>II</sup>, R<sup>III</sup>, R<sup>IV</sup> and R<sup>V</sup>, same or different, are H or linear or branched alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, provided that R and R<sup>I</sup> are not both H or CH<sub>3</sub> or are not CH<sub>3</sub> and n-propyl; R<sup>VI</sup> and R<sup>VII</sup> the same or different, are linear or branched alkyl, cycloaliphatic, aryl, or arylalkyl radicals having 1-18 carbon atoms; one or more of R to R<sup>VII</sup> may be bonded to form a cyclic structure.

The diethers are particularly useful in the preparation of Ziegler-Natta catalysts.